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Cited references:

JP Patent Application Disclosure No. 50-43913 (JP, A)

JP Patent Application Disclosure No. 62-20237 (JP, A)

JP Patent Utility Model Disclosure No. 50-79379 (JP, U)

JP Patent Utility Model Disclosure No. 7-42152 (JP, U)

Title: Light emitting diode

[Claims]

[Claim 1] Light emitting diode, comprising an LED chip arranged within a cup of mount lead, wherein a light emitting layer is composed of a gallium nitride-based compound semiconductor, an inner lead being electrically connected to said LED chip by a conductive wire, a coating member filling the inside of said cup with a translucent resin containing fluorescent material which is excited by the light emitted from said LED chip and emits light, and a mould member covering

said coating member, said LED chip, said conductive wire, and the top of said mount 1 ad as well as said inner lead, characterised in that
said LED chip emits a monochromatic peak wavelength within an emission spectrum of 400 nm to 530 nm,
said fluorescent material is $\underline{(RE_{1-x}Sm_x)_3 (Al_yGa_{1-y})_5O_{12}:Ce}$, and
the light from said LED chip and the light from said fluorescent material are capable of emitting white-series light by passing through said mould member, providing that $\underline{0 \leq x < 1, 0 \leq y \leq 1}$, <u>and RE is at least one selected from Y and Gd</u>.

[Claim 2] Light emitting diode according to Claim 1, wherein said mould member is of shape exhibiting a lens effect and contains a diffuser.

[Claim 3] Light emitting diode according to Claim 1, wherein said translucent resin is at least one selected from epoxy resin, urea resin and silicone.

[Claim 4] Light emitting diode according to Claim 1, wherein said mould member employs the same member as said translucent resin constituting said coating member.

[Claim 5] Light emitting diode according to Claim 1, wherein the fluorescent material is gradually increased from the surface side of said coating portion to the LED chip side.

[Claim 6] Light emitting diode, comprising an LED chip arranged within casing of chip-type LED, wherein a light emitting layer is composed of <u>a gallium nitride-based compound semiconductor</u>, and a mould member filling said casing, in which said LED chip is arranged, with a translucent resin containing

fluorescent material, which is excited by the light emitted by said LED chip and emits light, characterised in that
said LED chip emits a monochromatic peak wavelength within an emission spectrum of 400 nm to 530 nm,
said fluorescent material is $(RE_{1-x}Sm_x)_3(Al_yGa_{1-y})_5O_{12}:Ce$, and
the light from said LED chip and the light from said fluorescent material are capable of emitting a white-series light by passing through said mould member, providing that $0 \le x < 1$, $0 \le y \le 1$, and RE is at least one selected from Y and Gd.

[Detailed explanation of the invention]

[0001]

[Technology field of the invention]

The present invention relates to light-emitting diode utilised for LED display, light source for back light, traffic signal, illuminating switch, and various indicators; in particular to light-emitting diode of high-intensity and high-efficiency device, having a photoluminescence fluorescent material converting light emission from an LED chip as luminous element in order to emit the light, and being capable of emitting white light independently of use conditions

[0002] The light-emitting diode (hereinafter also designated as LED) is compact and efficient and emits brilliant light. Since it is a semiconductor element, there is no care of, such as burn-out of bulb. It has good initial drive characteristic, high vibration resistance and durability to endure repetitive ON/OFF operations. Accordingly, it is widely employed for various indicators and various light sources. Recently, light-emitting diodes as ultra-high-intensity and high-efficiency light-emitting diode, such as RGB (red, green and blue), have been developed, whereby the LED display employing three primaries RGB is

rapidly progressing, taking the advantage of operation with less power, long life and light weight.

[0003] Depending on employed semiconductor material of light-emitting layer and formation condition , the light-emitting diode is capable of releasing various light-emission wavelengths, from ultraviolet to infrared. It also has an excellent monochromatic peak wavelength.

[0004] Nevertheless, because the light-emitting diode has an excellent monochromatic peak wavelength, LED chips capable of emitting RGB respectively, being close to each other, must emit light, [the colours] must be diffused and mixed in order to be white-series light emission light surface. Such light-emitting diode is effective as light-emission device in order to emit lights of various colours freely, but even in case of emitting [single] colour like white-series, light-emitting diodes of red-series, green-series and blue-series, or light-emitting diodes of bluish green-series and yellow-series respectively must be employed. Because the LED chip is semiconductor, colour tone and intensity are still considerably various. In case of that the LED chips as semiconductor light-emitting device are made of different materials, initial drive power of each LED chip differs, so that power source must be ensured. For that reason, electric current or the like must be adjusted for each semiconductor in order to emit white-series. Similarly, since it is semiconductor light-emitting element, difference of individual temperature characteristics and changes through passage of time differ, so that the colour tone variously changes. Further, if the light emitted from LED chip uniformly colour-mixed, or colour-spotty occurs sometimes.

[0005] Accordingly, the present applicants previously have developed light-emitting diodes as light-emitting diode wherein the light-emission colour of LED

chip is colour-converted by fluorescent material, as disclosed JP Patent Application Disclosure No. 5-152609, JP Patent Application Disclosure No. 7-99345, etc. By those light-emitting diodes, another emission colour, such as white-series, can be emitted by means of a single kind of LED chip.

[0006] Specifically, an LED chip with a large energy band gap of a light emitting layer is arranged on the cup mounted at the top of lead frame. The LED chip is electrically connected to a metal stem and a metal post, where LED chips are mounted, respectively. [The light-emitting diode] is formed by that a fluorescent material absorbing the light from the LED chip and converting the wavelength is contained in a resin mould resin member or the like which covers the LED chip.

[0007] As light-emitting diode converting the wavelength of the emission from an LED chip, there is possible a light-emitting diode capable of emitting white-series by light-emission from blue-series light-emitting diode, absorbing the emission, and colour-mixing with the emission from fluorescent material emitting yellow-series. Those light-emitting diodes can emit light with a sufficient intensity, even in the use as light-emitting diode emitting white-series.

[0008]

[Problems to be solved by the invention]

As fluorescent material excited by light-emitting diode, there are fluorescent dyestuffs, fluorescent pigments, and further various ones from organic and inorganic compounds. Some fluorescent materials converts the light-emission wavelength from a luminous element, from short wavelength to long wavelength; whereas some fluorescent materials converts, the light-emission wavelength from a luminous element, from long wavelength to short wavelength.

[0009] Nevertheless, in case of conversion from long wavelength to short wavelength, the conversion rate is considerably poor, and is not for practical use. The fluorescent material arranged being close to LED chip is exposed to the ray with a strong irradiation intensity which is ca. 30-fold to 40-fold of sunlight. In particular, in case using an LED chip as luminous element and reducing the conversion rate improvement of a fluorescent material and the incorporation amount of fluorescent material, even if the light emitted from the LED chip lies within the visible radiation region, the light energy necessarily increases. In that case, if the light-emission intensity is further increased and [the light-emitting diode] is employed for the long term, the fluorescent material itself is susceptible to degradation. When the fluorescent material is degraded, sometimes the colour tone may shift, or the fluorescent material may be darken, so that the external takeoff efficiency of the light may be lowered. Similarly, a fluorescent material mounted close to LED chip is exposed to high temperature, e.g. an elevated temperature of the LED chip and heating from external environment. Further, although in general the light-emitting diode is coated by resin mould, it cannot completely prevent invasion of moisture from the external environment or cannot completely remove moisture stuck during the preparation. In some fluorescent materials, such moisture may stimulate the degradation of the fluorescent materials by high energy light from a luminous element and heat. In the ionic organic dyestuffs, there is a possibility that electrophoresis is effected by means of direct current electric field around the chip and the colour tone changes. Accordingly, the present invention purposes solution of said problems, to provide light-emitting diode with considerably less reduction of luminous efficacy and colour shift even under use conditions of high intensity for a long hour.

[0010]
[Means for solution of the problems]

The light-emitting diode according to Claim 1 comprises an LED chip arranged within a cup of mount lead, wherein a light emitting layer is composed of a gallium nitride-based compound semiconductor, an inner lead being electrically connected to said LED chip by a conductive wire, a coating member, which is a translucent resin containing fluorescent material which is excited by the light emitted from said LED chip and emits light, filled within the cup, and a mould member covering said coating member, said LED chip, said conductive wire, and a mould member covering at least part of the mount lead and inner lead. A light-emission spectrum of the LED chip is of monochromatic peak wavelength with an emission spectrum of 400 nm to 530 nm. The fluorescent material is $(RE_{1-x}Sm_x)_3(Al_yGa_{1-y})_5O_{12}:Ce$, providing that $0 \leq x < 1$, $0 \leq y \leq 1$, and RE is at least one selected from Y and Gd. The light from said LED chip and the light from said fluorescent material are capable of emitting white-series light by passing through said mould member.

[0011] Light emitting diode according to Claim 2 employs a mould member of shape exhibiting a lens effect. Light emitting diode according to Claim 3 employs a translucent resin which is at least one selected from epoxy resin, urea resin and silicone.

[0012] Light emitting diode according to Claim 4 employs, as mould member, the same member as said translucent resin constituting the coating member.

[0013] In light emitting diode according to Claim 5, fluorescent material of coating portion is gradually increased from the surface side to the LED chip side.

[0014] Further, light emitting diode according to Claim 6 comprises an LED chip and a mould member. In the LED chip, a light emitting layer

arranged within casing of chip-type LED is composed of a gallium nitride-based compound semiconductor. The mould member is a transparent resin filled within a casing arranging an LED chip, and contains fluorescent material, which is excited by the light emitted by the LED chip and emits light. The emission spectrum of the LED chip exhibits a monochromatic peak wavelength with emission peak from 400 nm to 530 nm. The fluorescent material is $(RE_{1-x}Sm_x)_3(Al_yGa_{1-y})_5O_{12}:Ce$, providing that $0 \leq x < 1$, $0 \leq y \leq 1$, and RE is at least one selected from Y and Gd. The light from the LED chip and the light from the fluorescent material are capable of emitting a white-series light by passing through said mould member.

[0015]

[Mode of application of the invention]

As result of various tests, the present inventors have found that in light-emitting diode colour-converting the light emitted from the LED chip with relatively high light energy within the visible radiation region by means of a photoluminescence fluorescent material, the reduction of luminous efficacy and colour shift in use of high intensity for a long hour can be prevented by choice of a certain semiconductor and fluorescent material, and led to the present invention.

[0016] In other words, LED chip employed for light-emitting diodes requires the following:

1. Stability of light-emission characteristic of the LED chip vis-à-vis the use for a long term;

2. Capability to emit efficiently a monochromatic peak wavelength with a high intensity and high energy sufficient for the excitation of the fluorescent material and secondary release.

The photoluminescence fluorescent material employed for light-emitting diodes requires the following advantageous characteristics:

1. Excellent light-resistance. In particular, due to an intensive irradiation from a micro-region, e.g. semiconductor luminous element, [the LED chip] must sufficiently endure a strong irradiation intensity which is ca. 30-fold to 40-fold of sunlight.

2. For the utilisation of colour mixture with luminous element, efficient light-emission by blue-series emission instead of ultraviolet light.

3. Light-emission capability of green-series to red-series light in consideration of colour mixture.

4. A good temperature characteristic for the arrangement in the neighbour of the luminous element.

5. Continuos variability of the colour tone by a composition proportion or by a mixing ratio of plurality of fluorescent materials.

6. Weather resistance depending utilisation environment of the light-emitting diode.

[0017] The present light-emitting diode satisfying those requirements is [composed of] the combination of a gallium nitride-based compound semiconductor element with a large energy band gap at a light emitting layer, and an yttrium aluminium garnet-based fluorescent material activated with cerium as photoluminescence fluorescent material, whereby even in case of that the high-energy light in the visible radiation region released from a luminous element is irradiated in the neighbour for a long time in high-intensity, a light-emitting diode with considerably less colour shift of emitted colour and less reduction of light-emission intensity becomes possible. In particular, the blue emission of InGaN as nitride-based compound semiconductor quite well corresponds with the absorption spectrum of an yttrium aluminium garnet-based fluorescent material activated with cerium. Mixture of the fluorescence of the yttrium aluminium garnet-based fluorescent material activated with cerium and the blue light of

InGaN exhibits quite particular performance not seen in other combination, in respect of gaining white of good quality with good colour rendering property.

[0018] Fig. 1 indicates a specific example of the light-emitting diode, and further Fig. 2 indicates a cross-sectional view of a chip-type LED. An LED chip 202 using gallium nitride-based semiconductor is fastened within casing 204 of the chip-type LED by means of epoxy resin or the like. Gold wire as conductive wire 203 is electrically connected to electrodes of the LED chip and to electrodes 205 mounted in the casing. [A member] wherein fluorescent material $(RE_{1-x}Sm_x)_3(Al_yGa_{1-y})_5O_{12}$:Ce is incorporated and dispersed in epoxy resin is formed by uniform setting as mould member 201 protecting the LED chip and the conductive wire from external stress. By electric power supply to such light-emitting diode, light-emission of the LED chip 202 is effected. A light-emitting diode capable of emitting white-series becomes possible by colour mixture of luminescence from the LED chip 202 and luminescence light from a photoluminescence fluorescent material excited by the [former] luminescence. Hereinafter, constitutional members of the present invention are illustrated.

[0019]

(Fluorescent material)

Fluorescent material employed for the present light-emitting diode is photoluminescence fluorescent material excited by visible light and ultraviolet light emitted from a semiconductor light-emitting layer, and emitting light. The photoluminescence fluorescent material is yttrium aluminium garnet-based fluorescent material activated by cerium.

[0020] In the present specification, the yttrium aluminium garnet-based fluorescent material should be interpreted particularly in broader sense. [Said fluorescent material] is employed in the broad sense by including such fluorescent

material, wherein a part of or whole of yttrium is substituted by at least one element selected from the group consisting of Lu, Sc, La, Gd and Sm, or alternatively a part of or whole of aluminium is substituted by one or both of Ga and In.

[0021] More specifically, [said yttrium aluminium garnet-based fluorescent material] is $(RE_{1-x}Sm_x)_3(Al_yGa_{1-y})_5O_{12}$:Ce (providing that $0 \leq x < 1$, $0 \leq y \leq 1$, and RE is at least one selected from Y and Gd). In case of that the light emitted from an LED chip employing gallium nitride-based compound semiconductor and the light emitted from photoluminescence fluorescent material whose body colour is yellow are in complementary colour relation, colour-mixture display of the luminescence from the LED chip and the luminescence from the photoluminescence fluorescent material enable the luminescence display of white-series. For that, at the light-emitting diode exterior, the luminescence from the LED chip and the luminescence from the photoluminescence fluorescent material must pass through the mould member. Accordingly, a light-emitting diode is acceptable, wherein an LED is enclosed in a fluorescent layer or the like, wherein the photoluminescence fluorescent material is formed by spattering method or the like, and the photoluminescence fluorescent material has at least one opening transmitting the light from LED chip, or is a film capable of transmitting the light from LED. The fluorescent material formed by spattering method or the like can omit binder in coating portion. The light-emission colour can be adjusted by the film thickness. Powder of photoluminescence fluorescent material is contained in resin or glass, [the mixture] is thinly moulded in such degree that the light from LED chip passes through. Similarly, powder of photoluminescence fluorescent material is contained in resin or glass, [the mixture] thinly moulded in such degree that the light from LED chip passes through. [sic] Any desired colour tone including white and incandescent lamp colour can provided by variously adjusting proportion of photoluminescence

fluoroscent material and resin or the like, applicatoin- or filling-amount, and by selecting luminous wavelength of luminous element.

[0022] Further, incorporation distribution of the photoluminescence fluoroscent material influences also the colour-mixture and durability. In other wordds, when the distribution concentration of the photoluminescence fluoroscent material is increased from coating portion and surface side of mould member towards LED chip, it is less susceptible to the influence of moisture from external environment, and degradation by moisture is easily suppressed. On the other hand, when the distribution concentration of the photoluminescence fluoroscent material is increased from LED chip towards mould member surface side, it is susceptible to the influence of moisture from external environment, but influence, such as fever from LED chip and irradiation intensity, is less, and degradation of the photoluminescence fluoroscent material can be suppressed. Such distribution of photoluminescence fluoroscent material can be variously formed by adjustment of member containing photoluminescence fluoroscent material, formation temperature, viscosity, shape of photoluminescence fluoroscent material, and particle distribution. ccordingly, the distribution concentration of fluoroscent material can be variously chosen depending on the use condition.

[0023] Photoluminescence fluoroscent material of the present light-emitting diode is in particular in contact with, or closely arranged to LED chip, and is sufficiently light-durable in high efficiency under an irradiation intensity of (Ee) = $3W \cdot cm^{-2}$ or less, so that a light-emitting diode with an excellent luminous characteristic is possible.

[0024] Due to garnet structure thereof, photoluminescence fluoroscent material employed for the present invention is durable to heat, light and moisture, and as Fig. 4 indicates, the excitation spectrum peak of around 450 nm is possible.

As Fig. 4 indicates, also the luminous peak lies around 580 nm, and [the photoluminescence fluoroscent material] has a broad light-emission spectrum with lower slope upto 700 nm.

[0025] By incorporation of Gd (gadolinium) in crystal, photoluminescence fluoroscent material of the present light-emittind diode can increase excitation luminous efficacy of the long wavelength region of 460 nm or higher. By the increase of Gd incorporation amount, the luminous peak wavelength is shifted to long wavelength, and the total luminous wavelength also is shifted to long wavelength. In other words, the necessity of luminous colour with strong red can be achieved by increasing substitution amount of Gd. On the other hand, with increase of Gd, the luminous intensity of photoluminescence by blue light tends to decrease.

[0026] Moreover, the luminous wavelength is shifted to long wavelength side by substituting a part of component Y by Gd, of the composition of yttrium aluminium garnet-based fluorescent material with garnet structure.

[0027] In the substitution of Al by Ga, in consideration of luminous efficacy and luminous wavelength, it is preferable to set a ratio Al:Ga = from 6:4 to 1:1. Likewise, the substitution of a part of Y by Gd is preferably set to a proportion Y:Gd = in the range of 9:1 to 1:9, morepreferably in the range of 4:1 to 2:3. With less than 20 % of substitution to Gd, green component becomes greater and red component less. With 60 % or more of substitution to Gd, although reddish component increases, the intensity tends to decrease drastically. In particular, depending on the luminous wavelength of LED chip, by Y:Gd = in the range of 4:1 to 2:3 among the composition of yttrium aluminium garnet-based fluorescent material, a light-emitting diode capable of emitting white light approximately along blackbody radiation trail is possible using a single kind of yttrium

aluminium garnet-based fluorescent material. With Y:Gd = higher than 2:3 to 1:4, although the intensity is lowered, a light-emitting diode capable of emitting incandescent lamp colour is possible. With incorporating 0.003 to 0.2 of Ce incorporation (substitution), relative luminous intensity becomes 70 % or higher. (The relative luminous intensity is a luminous intensity when the luminous intensity of a fluorescent material with q = 0.03 is 100 %.) With less than 0.003, the intensity lowers due to reduction of the number of excitation luminous centre of photoluminescence by Ce. On the contrary, with higher than 0.2, density extinction occurs. (The density extinction means that with increase of activator concentration in order to increase the intensity of fluorescent material, the luminous intensity decreases at concentrations higher than an optimal value.

[0028] With the photoluminescence fluoroscent material the present light-emitting diode can continously adjust the luminous colour by such variation of the composition. It is scarcely excited by Hg luminescent line of 254 nm or 365 nm, and the excitation efficiency by the light from blue-series LED chip is high. Accordingly, [the fluoroscent material] has ideal requirements for converting the blue-series luminescence of nitride semiconductor into white-series luminescence, eg.. that the intensity of long wavelength side is continuously varied by composition proportion of Gd.

[0029] Table 1 indicates an example of the composition of photoluminescence fluoroscent material and luminous characteristic. (The measurement condition is that it was excited by blue light of 460 nm and measured. The intensity and efficiency are expressed by relative values.)

[0030]

[Table 1]

フォトルミネッセンス蛍光体の組成	CIE色度座標		輝度	エネルギー効率
	x	y	Y	ENG
$Y_3Al_5O_{12}:Ce$	0.41	0.56	100	100
$Y_3(Al_{0.6}Ga_{0.4})_5O_{12}:Ce$	0.32	0.56	61	63
$Y_3(Al_{0.5}Ga_{0.5})_5O_{12}:Ce$	0.29	0.54	55	67
$(Y_{0.8}Gd_{0.2})_3Al_5O_{12}:Ce$	0.45	0.53	102	108
$(Y_{0.6}Gd_{0.4})_3Al_5O_{12}:Ce$	0.47	0.52	102	113
$(Y_{0.4}Gd_{0.6})_3Al_5O_{12}:Ce$	0.49	0.51	97	113
$(Y_{0.2}Gd_{0.8})_3Al_5O_{12}:Ce$	0.50	0.50	72	86

Composition of photoluminescence fluoroscent material	CIE chromaticity coordinate		Intensity Y	Energy efficiency ENG
	x	y		

....

[0031] Light efficiency can be further improved by light-emitting diode comprising an LED chip employing a gallium nitride-based semiconductor, and a photoluminescence fluoroscent material wherein rare earth element samarium (Sm) is incorporated with an yttrium aluminium garnet fluorescent material (YAG) activated with cerium.

[0032] Raw material for such photoluminescence fluoroscent material is obtained by that oxides thereof as raw materials for Y, Gd, Ce, Sm, Al and Ga, or compounds easily becoming oxides at high temperature are sufficiently mixed in a stoichiometric ratio. Alternatively, a solution wherein rare earth elements Y, Gd, Ce and Sm in a stoichiometric ratio are dissolved in acid is coprecipitated with oxalic

acid, the coprecipitate is calcined, the obtained coprecipitation oxides, aluminium oxide and gallium oxide are mixed to provide raw material mixture. A suitable amount of fluoride, such as ammonium fluoride, is incorporated with this

mixture, [the mixture] is placed in a crucible, is calcined in the air at temperature range of 1350 to 1450 °C for 2 to 5 hours to provide calcined product, subsequently the calcined product is subjected ball milling in water, washed, separated, dried and finally sieved, whereby [the photoluminescence fluoroscent material] is obtainable.

[0033] Fluoroscent material $(Y_{1-p-q-r}Gd_pCe_qSm_r)_3\ Al_5O_{12}$ containing Sm exhibits less decrease of temperature characteristic, regardless of increase of Gd incorporation amount. Such incorporation of Sm drastically improves the luminous intensity of photoluminescence fluoroscent material at high temperature. The more Gd incorporation amount, the larger the improvement degree. In other words, it was found that the composition red-imparted to the luminous colour tone of photoluminescence fluoroscent material by increase of Gd is effective to the temperature characteristic improvement by Sm incorporation. (In this context, the temperature characteristic is expressed by relative value (%) of luminous intensity of the fluorescent material at a high temperature (200 °C) vis-à-vis excitation luminous intensity at normal temperature (25 °C) by blue light of 450 nm.)

[0034] Preferable incorporation amount of Sm is $0.0003 \leq r \leq 0.09$ which allows the temperature characteristic 60 % or higher. With r less than the range, the effect of temperature characteristic improvement becomes less. With r more than the range, on the contrary the temperature characteristic lowers. With the range of $0.0007 \leq r \leq 0.02$, the temperature characteristic becomes 80 % or more, which is most preferable.

[0035] In the present light-emitting diode, such photoluminescence fluoroscent material may be a mixture of at least two $(RE_{1-x}Sm_x)_3\ (Al_yGa_{1-y})_5O_{12}$:Ce photoluminescence fluoroscent materials. In other words, wevelength

components of RGB can be increased by mixing at least two $(RE_{1-x}Sm_x)_3(Al_yGa_{1-y})_5O_{12}$:Ce photoluminescence fluoroscent materials with different incorporation amounts of Al, Ga, Y and Gd as well as Sm. Colour filter is applied to this, whereby it is alsoutilised for liquid crystal display device.

[0036]

(LED chip 102, 202, 702)

As Fig. 1 indicates, LED chip is embedded in mould member 104. The LED chip employed for the present light-emitting diode is nitride-based compound semiconductor capable of efficiently exciting an yttrium aluminium garnet-based fluorescent material activated with cerium. In this context, the nitride-based compound semiconductor (general formula $In_iGa_jAl_kN$, wherein $0 \leq i$, $0 \leq j$, $0 \leq k$, $i+j+k = 1$) includes various ones, e.g. InGaN and GaN to which various impurities are doped. LED chip as luminous element is formed on the substrate wherein semiconductor, such as InGaN, is a luminous layer, by MOCVD method or the like. As structure of the semiconductor, there are homo strucutre, hetero structure or double hetero structure having MIS junction, PIN junction and PN junction. In line with materials of semiconductor layer and mixed crystal degree thereof, the luminous wavelength can be variously chosen. Alternatively, [the semiconductor structure] may be single quantum well structure or multiple quantum well structure wherein a semiconductor active layer is formed on a film generating quantum effect. In particular, in the present invention, by that an active layer of LED chip is single quantum well structure of InGaN, [the structure] is utilisable as a light-emitting diode emitting in higher intensity without degradation of photoluminescence fluoroscent material.

[0037] In the use of gallium nitride-based compound semiconductor, materials, such as sapphire, spinel, SiC, Si, ZnO, etc., are employed for semiconductor substrate. In order to form gallium nitride with a good

crystallinity, the use of sapphire substrate is preferable. A buffer layer composed of GaN, AlN, etc. is formed on this sapphire substrate, on which gallium nitride semiconductor with PN junction is formed. The gallium nitride semiconductor without doping impurities exhibits N-type conductivity. In case of forming a desired N-type gallium nitride semiconductor, e.g. improvement of luminous efficacy, suitable introduction of Si, Ge, Se, Te, C, etc. as N-type dopant is preferred. On the other hand, in formation of P-type gallium nitride semiconductor, Zn, Mg, Be, Ca, Sr, Ba, etc. as P-type dopant are doped. Since the gallium nitride-based compound semiconductor is not easily converted to P-type simply by doping the P-type dopant; after introduction of P-type dopant, it is preferably converted to P-type by heating in furnace, low-energy electron beam irradiation, plasma irradiation, etc. Exposure surface of P-type semiconductor and N-type semicoductor is formed by etching or the like, and subsequently electrodes of any desired shape are formed on the substrate layer by spattering method, vacuum evaporation method, etc.

[0038] Next, thus formed semiconductor wafer is directly full-cut off by a rotating dicing saw with an edge made of diamond; or alternatively after cut into groove with a width wider than the edge width (half cut), the semiconductor is divided by external force. Alternatively, considerably fine scribe-line (meridian), e.g. tessellated, is drawn by a scriber wherein diamond needle of the top does linear reciprocating motion, and subseqently the wafer is divided by external force, and chips are cut out from the semiconductor wafer. In such manner, LED chip as gallium nitride-based compound semiconductor can be formed.

[0039] In case of that the present light-emitting diode emits white-series, in consideration of in complementary colour relation with photoluminescence fluorescent material and resin degradation, the luminous wavelength of luminous

element is preferably 400 nm or higher to 530 nm or less, more preferably 420 nm or higher to 490 nm or less. In order to improve effciencies of LED chip and photoluminescence fluorescent material, 450 nm or more to 475 nm or less is more preferable. Luminous spectrum of the present white-series light-emitting diode is shown in Fig. 3. The luminescence with a peak around 450 nm is luminescence from LED, whereas the luminescence with a peak around 570 nm is luminescence of photoluminescence material excited by the LED chip. In addition to the present LED chip, an LED chip not exciting the fluorescent material may be simultaneously employed.

[0040] Specifically, in addition to LED chip as nitride-based compound semiconductor which can excite the photoluminescence fluorescent material, an LED chip, wherein a luminous layer substantially not exciting the photoluminescence fluorescent is gallium phosphorus, gallium aluminious arsenic, gallium arsenic phosphorus or indium gallium aluminium arsenic, is arranged. The light from the LED chip no exciting photoluminescence fluorescent material, not being absorbed by the fluorescent material itself, is released outside. Accordingly, a light-emitting diode capable of efficiently emitting red-and-white is possible.

[0041]

(Conductive wire 103, 203)

As conductive wire 103, 203, the one with good ohmic property with electrodes of LED chip 102, 202, mechanical connection, electric conductivity and thermal conductivity are required. Thermal conductivity is preferably 0.01 cal/(s)(cm^2)(°C/cm) or higher, more preferably 0.5 cal/(s)(cm^2)(°C/cm) or higher. In consideration of workability, diameter of the conductive wire is preferably at least Φ 10 μm, at most Φ 45 μm. In particular, the conductive wire susceptible to breakage at the interface between the coating portion containing

fluoroscent material and the mould member free from fluoroscent material. It is considered that even if the wires employ identical material, substantial thermal expansion quantities differ by incorporation of fluoroscent material, so that the wire is susceptible to breakage. Consequently, the diameter of the conductive wire is preferably at least 25 μm; in view of luminescence surface area and easy handling, is more preferably at most 35 μm. Such conductive wires are specifically conductive wire made of metals, such as gold, copper, platinum, aluminium, etc., and alloys thereof. Such conductive wire can be easily connected to electrodes of LED chips, inner lead and mount lead, by means of wire bonding device.

[0042]

(Mount lead 105)

Any one, which arranges LED chip 102 and has a sufficient size sufficient for mounting by die bonding device or the like, is acceptable as mount lead 105. In case of that a plurality of LED chip is mounted and the mount lead is employed as common electrodes of the LED chips, a sufficient electric conductivity and connectivity to bonding wire are required. In case of that LED chip is arranged within a cup on the mount lead and simultaneously the inside is filled with fluorescent material, it can prevent pseudo-lightening by the light from another light-emitting diode.

[0043] The adhesion between LED chip 102 and the cup of mount lead 105 can be effected by thermosettable resin or the like. Specific resins are epoxy resin, acryl resin, imide resin, etc. Ag paste, carbon paste, metal bump, etc. are employable for adhesion to mount lead by face down LED chip and simultaneous electrical connection. Further, for the improvement of light utilisation efficiency of light-emitting diode, the surface of the mount lead may be mirror-like, so that the surface has reflect ability. In that case, the surface roughness is preferably at

least 0.1 S to at most 0.8S. Concrete electric resistance of the mount lead is preferably at most 300 μΩ-cm, more preferably at most 3 μΩ-cm. In case of that a plurality of LED chip is mounted on the mount lead, a good thermal conductivity is required for the more calorific value from LED chip. Specifically, [the thermal conductivity] is at least 0.01 cal/(s)(cm^2)(°C/cm), more preferably at least 0.5 cal/(s)(cm^2)(°C/cm). As materials satisfying those requirements, there are iron, copper, iron-containing copper, tin-containing copper, ceramic with metallise pattern, etc.

[0044]

(Inner lead 106)

Inner lead 106 is connected to the conductive wire 103 which is connected to the LED chip 102 mounted on the mount lead 105. When a plurality of LED chips are mounted on the mount lead, conductive wires must be arranged such that they do not contact each other. For that purpose, the area of the end face where the inner leads are wire-bonded may be increased as the distance from the mount lead increases, for example. Surface roughness of the inner lead end face connecting with the conductive wire is preferably from 1.6S to 10S inclusive in consideration of close contact. A desired shape of the inner lead end face can be formed by punching, or it may be obtained by grinding part of the upper portion of the inner lead after all the necessary inner leads have been made. Alternatively, a desired edge-surface area and edge surface height may be simultaneously obtained by pressing the end face vertically after punching out the inner lead.

[0045] The inner lead is required to have good connectivity with the bonding wires which are conductive wires and have good electrical conductivity. Specifically, the electric resistance is preferably within 300μΩ-cm and more preferably within 3μΩ-cm. Materials which satisfy these requirements contain

iron, copper, iron-containing copper, tin-containing copper, copper-, gold- or silver-plated aluminum, iron and copper.

[0046]

(Coatig portion 101)

Coating portion 101 employed for the present invention is settled in a cup of mount lead, and contains photoluminescence fluoroscent material converting luminescence of LED chip. As specific material of the coating portion, there are suitably employed transparent resins with excellent weather resistance, such as epoxy resin, urea resin, silicone, etc., and glass. Together with photoluminescence fluoroscent material, diffuser may be incorporated. As specific diffuser, there are suitably employed barium titanate, titanium oxide, aluminium oxide, silicon oxide, etc.

[0047]

[Mould member]

(Mould member 104)

Depending on the utilisation purpose of light-emitting diode, mould member 104 may be prepared in order to protect LED chip 102, conductive wire 103, coating portion 101 containing photoluminescence fluoroscent material, etc. from external environment. In general, the mould member may be formed using resin. The visible angle can be increased by incorporation of photoluminescence fluoroscent material, and the visible angle can be more increased by incorporation of diffuser with resin mould to relieve the directivity from LED chip 102. Further, by any desired shape of the mould member 104, the lens effect focusing or diffusing the luminescence from LED can be provided. Accordingly, the mould member 104 may be structure of plural lamination. Specifically, it is convex lens shape, concave lens shape, and elliptical shape seen

from luminescence observation side, and combination of thereof. As specific material for mould member 104, there are suitably employed mainly transparent resins with excellent weather resistance, such as epoxy resin, urea resin, silicone resin, etc., and glass. As diffuser, there are suitably employed barium titanate, titanium oxide, aluminium oxide, silicon oxide, etc. Further, in addition to diffuser, photoluminescence fluorescent material can be contained also in mould member. Accordingly, the photoluminescence fluoroscent material may be incorporated in the mould member, or may be incorporated in other part, such as coating portion. [The mould member and the coating portion] may be formed by use of different members, e.g. the coating portion is resin containing photoluminescence fluoroscent material, whereas the mould member is glass. In that case, a light-emitting diode with good productivity and less influence of moisture is possible. In consideration of refractive index, the mould member and the coating portion may be formed by use of the same member. In the present invention, incorporation of diffuser and colourant with mould member can hide the colouring of fluorescent material seen from luminescence observation side. The colouring of fluorescent material means that the present photoluminescence fluorescent material absorbes blue light among lights from strong, external light, and emits light, so that [the fluorescent material] appears to be yellow-coloured. In particular, depending on the shape of mould member, e.g. convex lens shape, sometimes the coloured portion appears to be enlarged. Such colouring is sometimes not preferred in view of design. The diffuser incorporated with mould member can make the colouring not visible by that the mould member is coloured into opaque white and the colouring agent is coloured into any desired colour. Accordingly, colour of photoluminescence fluorescent material is not observed from such luminescence observation side. With at least 430 nm of main fluorescence wavelength of the light released from LED chip, incorporation of ultraviolet light absorbant as light stabiliser in the mould member is rather preferable in view of weather resistance.

[0048]

(Display device)

In case of utilising the present light-emitting diode to LED display unit, it is possible to display white-series finer than the LED display unit composed of simple combination of light-emitting diodes emitting RGB respectively; because the conventional device displays white-series by use of three light-emitting diodes, whereas the device using the present light-emitting diode can display white by use of single light-emitting diode. In other words, for colour-mixture displaying of white-series by combination of light-emitting diodes, in the conventional display device, light-emitting diodes of RGB must emit light at the same time. Consequently, in comparison with monochromatic displaying of red-series, green-series and blue-series, the display region per pixel becomes larger. Accordingly, in case of displaying white-series, higly fine displaying is not possible in comparison with monochromatic displaying of RGB simple colours. Since the white-series is displayed by adjustment of luminous output of each light-emitting diode, various adjustment is necessary in consideration of temperature characteristic of each semiconductor. Further, due to displaying by colour mixture, by visual recognition direction or angle of the LED display unit, sometimes light-emitting diodes of RGB may partially shielded and displaying colour may change. The display device using the present light-emitting diode in place of light-emitting diodes of RGB has advantages, i.e. that it can emit stably white-series, and can decrease colour shading. The present light-emitting diode can be employed together with light-emitting diodes of RGB. This display device can improve the intensity.

[0049] LED display unit employing the present light-emitting diode is shown in Fig. 5. The LED display unit of this drawing is utilised for an LED display device for white-and-black using only the present white-series light-emitting

diode. The LED display unit for white-and-black arranges only the present light-emitting diode 501 in matrix form. The display device containing the LED display unit of this drawing does not have light-emitting diodes of RGB. Conseqeuntly, it does not require a plurality of driving circuits for RGB light-emitting diodes. In place of a plurality of driving circuits, a driving circuit for white-series light-emitting diode can drive the LED display unit.

[0050] The LED display is electrically connected to a lighting circuit as driving circuit, and so on. A display capable of displaying various images by output pulse from the driving circuit is possible. The driving circuit is shown in Fig. 6. The driving circuit comprises an RAM (random access memory) 603 as image data storage means, temporarily storing the input display data, a gradation control circuit 604 computing gradation signal in order to lighten each light-emitting diode of the LED display unit 601 in a certain brightness from the data stored by RAM 630, and a driver 602 switched by output signal of the gradation control circuit 604 in order to light the light-emitting diode. The gradation control circuit 604 computes the lighting time of light-emitting diode of LED display unit 601 to output pulse signal for blinking.

[0051] Therefore, the LED display unit for white-and-black can simplify and can highly fine the circuit constitution, differing from full-colour display unit of RGB. Accordingly, it can realise inexpensively a display without the circuit constitution accompanied by the characteristics of RGB light-emitting diodes. In comparison with the conventional LED display unit using red and green alone, irritation to human eyes is reduced and it is suitable for the use for a long time.

[0052] The present light-emitting diode as white light-emittingg diode (W) may be used being added to light-emitting diodes which emit RGB, as Fig. 8 indicates. In the drawing, symbol 900 indicates a part of LED display unit, and

900 constitutes one pixel. This LED display unit is electrically connected to lighting circuit as driving circuit. By output pulse from the driving circuit, a display capable of displaying various images is possible. Similar to the monochromic display device, the driving circuit comprises an RAM (random access memory) as image data storage means, temporarily storing the input display data, a gradation control circuit computing gradation signal in order to lighten each light-emitting diode in a certain brightness from the data stored by RAM, and a driver switched by output signal of the gradation control circuit in order to light the light-emitting diode. However, this driving circuit requires a circuit exclusive for light-emitting diodes emitting RGB and white-series. The gradation control circuit computes ligting time of each light-emitting diode from the data stored in RAM, in order to output pulse signal to be blinked. In case of dislaying white-series, pulse width of pulse signal lighting the light-emitting diodes of RGB is shortened, alternatively peak value of pulse signal is lowered, or alternatively pulse signal is not output at all. On the other hand, in order to compensate that, pulse signal is out to white-series light-emitting diode, whereby white of LED display unit is displayed.

[0053] Accordingly, it is preferable to provide a CPU as gradation control circuit computing the pulse signal in order to light white-series light-emitting diode in a desired intensity. The pulse signal output from the gradation control circuit is input to a driver of the white-series light-emitting diode, to switch the driver. When the driver is on, the white-series light-emitting diode is lighted; with off, the light is off.

[0054]

(Signaling device)

When the LED of the invention is used in a signaling device such as the traffic lights, which are a kind of display device, such advantages can be obtained as

stable illumination over a long period of time and no color unevenness even when part of the LEDs go out. A white light signaling device can be made as follows. White light emitting diodes are arranged on a substrate whereon a conductive pattern is formed. The LEDs are connected in series and/or parallel to form two or more groups of the LEDs. In each group, the LEDs are spirally arranged. Thus, the LEDs are arranged over the entire area in circular configuration. Power lines by soldering for the connection of the LEDs and the substrate with external power supply are soldered and fastened in a railway signal housing. The LED display device is placed in an aluminum diecast housing equipped with a light blocking member and is sealed on the surface with silicon rubber filler. The housing is provided with a white color lens on the display plane thereof. Electric wiring of the LED display device is passed through a rubber packing on the back of the housing, and the housing is sealed. In this signaling device, since the LEDs are divided into a plurality of groups, and spirally arranged from the center toward the outside while being connected in parallel, a high degree of reliability can be ensured. The spiral configuration may be either continuous or intermittent so that the number of the LEDs or groups of LEDs can be chosen as desired, depending on the display area of the LED display device. Furthermore, even when one of the groups of LEDs or part of the LEDs fail to illuminate due to some trouble, uniform, circular illumination can be emitted by the remaining groups of LEDs or remaining LEDs without color shift. Because of the spiral configuration, the LEDs can be more densely provided near the center, so that the signaling device can be operated without giving any different impression from the signaling devices employing incandescent lamps.

[0055]

(Surface illuminant)

The present light-emitting diode may be surface illuminant, as Fig. 7 indicates. The light-emitting diode of the surface illuminant shown the drawing allows a

phosoluminescence fluorescent material being incorporated with coating portion and with scattering sheet 706 on the light guiding plate. Alternatively, [the phosoluminescence fluorescent material] together with binder resin is applied on a scattering sheet 706, moulded into sheet shape 701, and mould member may be omitted. Specifically, an insulating layer and LED chip is fastened within a metal substrate 702 of  shape wherein a conductivity pattern are formed. Electric conduction between LED chip and conductive pattern is made, subseqeuntly the photoluminescence fluorescent material is mixed with epoxy resin, and stirred, and [the mixture] is placed over metal substrate 703, to which LED chip 702 is mounted. Thus fastened LED chip is fastened on terminal surface of acryl light-guiding plate 704 by epoxy resin. Reflection member 707 of film containing white scattering agent for the prevention of firefly phenomenon is arranged on another main surface of the light-guiding plate 704. Similarly, reflective member 705 is provided on whole backside of the light-guiding plate and on terminal surface wherein LED is not arranged, whereby the luminous efficacy is improved. Thereby, a light-emitting diode as surface illuminant capable of obtaining a brightness sufficient to LCD backlight is possible. In utilisation as liquid crystal display device, it can be constituted by that polarlising plate arranged via liquid crystal device injected between glass substrates wherein a light-trasmittable conductive pattern, not shown in the drawing, is formed on the main surface of light-guiding plate 704. Hereinafter, examples of the present invention are illustrated. Not necessary to say, the present invention is not limited to specific examples.

[0056]

[Embodiments]

(Embodiment 1)

As the light emitting element, an InGaN semiconductor with an emission peak at 450nm and a half width of 30nm was used in the light emitting layer. An LED chip was made by flowing TMG (trimethyl gallium) gas, TMI (trimethyl indium) gas, nitrogen gas and dopant gas together with a carrier gas on a cleaned sapphire substrate and forming a nitride compound semiconductor layer by MOCVD process. While the layer is being formed, SiH4 and Cp2Mg as dopant gases are switched, thereby forming a gallium nitride semiconductor having N and P type conductivity. As the semiconductor light emitting element, a contact layer of gallium nitride semiconductor with N type conductivity, a clad layer of gallium nitride aluminum semiconductor with P type conductivity, and a contact layer with N type conductivity were formed. Between the contact layer with P type conductivity and the clad layer with P type conductivity was formed a non-doped InGaN activation layer of thickness about 3nm having a single quantum well structure. (The sapphire substrate has a gallium nitride semiconductor layer formed thereon under a low temperature which acts as a buffer layer. The P type semiconductor was annealed at a temperature of 400°C or above after film formation.)

[0057] After exposing the surfaces of P type and N type semiconductor layers by etching, corresponding electrodes were formed by sputtering. The semiconductor wafer thus prepared was scribed and then divided by external force, thereby obtaining LED chips as the light emitting elements.

[0058] The LED chip thus produced was die-bonded with epoxy resin in a cup of a mount lead formed by silver-plated copper lead frame. The electrodes of the LED chip, the mount lead and the inner lead were electrically connected by wire bonding with gold wires 30μm in diameter.

[0059] On the other hand, the photoluminescence phosphor was made as follows. Rare earth elements of Y, Gd and Ce were dissolved in an acid in stoichiometrical proportions. The solution was coprecipitated with oxalic acid. Oxide of the copreciptate obtained by firing this material was mixed with aluminum oxide, thereby obtaining a mixture material. The mixture was then mixed with ammonium fluoride used as a flux, and fired in a crucible at a temperature of 1400°C in air for 3 hours. The fired material was then ground by a ball mill in water, washed, separated, dried and sieved. Thus, the photoluminescence phosphor was prepared as yttrium-aluminum-oxide represented by the general formula (Y0.8Gd0.2)3Al5O12: Ce, where about 20% of Y is substituted with Gd and substitution ratio of Ce is 0.03.

[0060] Eighty parts by weight of the phosphor thus formed having a composition of (Y0.8Gd0.2)3Al5O12: Ce and 100 parts by weight of epoxy resin were sufficiently mixed to turn into slurry. The slurry was poured into the cup on the mount lead on which the LED had been mounted. After pouring, the resin containing the photoluminescence phosphor was cured at 130°C for one hour. Thus a coating containing the phosphor with a thickness of 120μm was formed on the LED. The coating was formed to contain the phosphor in gradually increasing concentration toward the LED chip. Irradiation intensity was about 3.5W/cm2. Thereafter, a molding member of translucent epoxy resin was formed for the purpose of protecting the LED chip and phosphor against extraneous stress, moisture and dust. The mold member was formed by first inserting the lead frame on which the coating of phosphor was formed and then mixing it with translucent epoxy resin, which was cured at 150°C for 5 hours. Under visual observation of the LED formed as described above in the direction normal to the light emitting plane, it was observed that the central portion was rendered yellowish color due to the body color of the phosphor.

[0061] The LED capable of emitting white light was measured for chromaticity point, color temperature and color rendering index, and values of (x=0.302, y=0.280) for chromaticity point, color temperature of 8080K and 87.5 for color rendering index (Ra) were obtained. These values are approximate to the characteristics of a 3-waveform fluorescent lamp. Light emitting efficiency was 9.5lm/W, comparable to that of an incandescent lamp. Further in life tests under conditions of energization with a current of 60mA at 25°C, 20mA at 25°C and 20mA at 60°C with 90% RH, no change due to the phosphor was observed, proving that the LED was not different in terms of service life from the conventional blue light emitting diode.

[0062]

(Comparative Example 1)

An LED was formed in the same manner as in Embodiment 1 except for the use of photoluminescence phosphor (ZnCd)S: Cu, Al instead of $(Y_{0.8}Gd_{0.2})_3Al_5O_{12}$: Ce, and the LED was tested for service life. The LED thus formed emitted white light as in Embodiment 1 after energization, but its luminance was low. In a life test, the output diminished to zero in about 100 hours. Analysis of the cause of deterioration showed that the fluorescent material was blackened.

[0063] This problem is supposed to have been caused as the light emitted by the light emitting component and moisture which caught on the phosphor or entered from the outside brought about photolysis to make colloidal zinc to precipitate on the surface of the phosphor crystal, resulting in blackened surface. Results of life tests under conditions of energization with a current of 20mA at 25°C and 20mA at 60°C with 90% RH are shown in Fig. 8 together with the results of Embodiment 1. Luminance is given in terms of relative value with respect to the

initial value as the reference. A solid line indicates Embodiment 1 and a broken line indicates Comparative Embodiment 1.

[0064]

(Embodiment 2)

One hundred LEDs were made in the same manner as in Embodiment 1 except for increasing the content of In in the nitride compound semiconductor of the LED chip to have the emission peak at 460nm and increasing the content of Gd in the phosphor than that of Embodiment 1 to have a composition of $(Y_{0.6}Gd_{0.4})_3Al_5O_{12}$: Ce.

[0065] The thus formed LEDs capable of emitting white light were measured for chromaticity point, color temperature and color rendering index. As a result, chromaticity point (x=0.375, y=0.370), color temperature of 4400K and color rendering index (Ra) of 86.0 were obtained. Service life test was conducted based on average luminous intensities of the LEDs after 1000 hours of use. In terms of percentage of the luminous intensity value before the life test, the average luminous intensity after the life test was 98.8%, proving no difference in the characteristic. The emission spectrum of the phosphor, the LED chip and the LED are shown in Fig. 10(A), (B), and (C), respetively.

[0066]

(Embodiment 3)

One hundred LEDs were made in the same manner as in Embodiment 1 except for adding Sm in addition to rare earth element y, Gd and Ce in the phosphor to make a phosphor with composition of $(Y_{0.39}Gd_{0.57}Ce_{0.03}Sm_{0.01})_3Al_5O_{12}$. When the LEDs were made to illuminate at a high temperature of 130°C, average temperature characteristic about 8% better than that of Embodiment 1 was obtained.

[0067]

(Embodiment 4)

The LEDs of Embodiment 1 were arranged in a 16x16 matrix on a ceramics substrate whereon a copper pattern is formed. The substrate and the LEDs were soldered by an automatic soldering machine. The substrate on which the LEDs were arranged was placed in a chassis 504 which is made of phenol resin and was provided with a light blocking member 505 formed integrally therewith. The chassis, the LEDs, the substrate and part of the light blocking member, except for the tips of the LEDs, were covered with silicon rubber 406 colored in black with a pigment. Thereafter, the silicon rubber was cured for 72 hours at room temperature, thereby obtaining an LED device. An LED display apparatus is formed by electrically connecting the thus constructed LED device, a RAM for temporarily storing the input display data, a tone control circuit for processing the data stored in the RAM to compute tone signals for lighting the LEDs with specified brightness, and drive means which is switched by the output signal of the tone control circuit to cause the LEDs to illuminate. The LED display apparatus was driven and observed to be able to function as a black and white LED display apparatus.

[0068]

(Embodiment 5)

One hundred LEDs were made in the same manner as in Embodiment 1 except for using phosphor represented by general formula (Y0.2Gd0.8)3Al5O12: Ce. Measurement of the chromaticity point gave values of (x=0.450, y=0.420; average values), and light of incandescent lamp color was emitted. Although the LEDs' luminance was about 40% lower than that of the LEDs of Embodiment 1, they showed good weatherability comparable to that of Embodiment 1 in life test.

The emission spectrum of the phosphor, the LED chip and the LED are shown in Fig. 11(A), (B), and (C), respetively.

[0069]

(Embodiment 6)

One hundred LEDs were made in the same manner as in Embodiment 1 except for using phosphor represented by general formula Y3Al5O12: Ce. Although the LEDs of Embodiment 6 emitted greenish white light with a low luminance, they showed good weatherability similar to that of Embodiment 1 in life test. The emission spectra of the phosphor, the LED chip and the LED are shown in Fig. 12 (A), (B) and (C), respectively.

[0070]

(Embodiment 7)

One hundred LEDs were made in the same manner as in Embodiment 1 except for using phosphor represented by general formula Y3(Al0.5Ga0.5)5O12: Ce. Although the LEDs of Embodiment 7 emitted greenish white light with a low luminance, they showed good weatherability similar to that of Embodiment 1 in life test. The emission spectra of the phosphor, the LED chip and the LED are shown in Fig. 13 (A), (B) and (C), respectively.

[0071]

(Embodiment 8)

One hundred LEDs were made in the same manner as in Embodiment 1 except for using phosphor represented by general formula Gd3(Al0.5Ga0.5)5O12: Ce which does not contain Y. Although the LEDs of this embodiment showed a low luminance, they showed good weatherability similar to that of Embodiment 1 in life test.

[0072]

(Embodiment 9)

One hundred LEDs were made in the same manner as in Embodiment 1 except for using a phosphor not containing Al, represented by the general formula $Y_3In_3O_{12}$: Ce. The LEDs of this embodiment had low luminance but showed good weatherability in life test comparable to that of Embodiment 1.

[0073]

(Advantageous effects of the invention)

The invention provides an LED which is formed by combining a light emitting element of gallium nitride semiconductor with a specific phosphor. The LED can provide high luminous efficiency for a long period of use at high luminance. The inventive LED can open up new lighting possibilities for automobiles, airplanes and other general electric appliances because of its reliability, low power consumption, small size and variable color temperature features. In particular, the photoluminescence phosphor used in the invention can be used as a light source having short afterglow with the response rate of 120nsec. The LED can be adapted to emit white light in order to allow visual observation over a long period of time without causing too much irritation to the eye. Although the LED chip has a monochromatic peak wavelength, it also has a spectrum width to some extent and hence a high degree of color rendering property, which is an advantage indispensable to a wide range of light source applications. Specifically, the LED can be used as a light source with wide spectrum width in a scanner, for example.

[0074] The LED according to the invention can emit white light for a long period of time at high luminance with only a little color displacement and reduction in luminous efficiency. Further, in accordance with the invention, reduction in luminanc as a result of resin degradation can be suppressed.

[0075] The LED in accordance with the invention can emit light efficiently. Generally speaking, phosphor has better efficiency when converting light from shorter wavelengths to longer wavelengths. It is also preferable in LEDs to use visible light than ultraviolet light because the latter degrades resin (when used as molding members or coating members). The invention utilizes blue light, which is on the shorter wavelength side of the visible light spectrum, and the blue light is further converted to light with even longer wavelengths efficiently. The converted light therefore has longer wavelength than that of the light emitted by the LED chip (In other words, the light energy emitted by the phosphor is smaller than the band gap of the LED chip). Accordingly, any light reflected or scattered by the photoluminescence phosphor towards the mount lead side, i.e., towards the non-emission observation side is not easily absorbed by the LED chip. Thus, even if part of the light converted by the photoluminescence phosphor was directed towards the LED chip, it would not be absorbed by the LED chip but instead reflected by the mount lead cup, for example, thereby allowing an efficient light emission.

[0076] Thus, the LED of the invention is capable of long period of use at high luminance with only a slight amount of color displacement and reduction in luminous efficiency. In addition, a number of the LEDs can be closely arranged without having light emitted by one LED excite the phosphor of another LED such that the another LED emits false light. Because the inherent emission unevenness of the LED chip can be spread by the phosphor, emission uniformity of the LED can be improved. Normally, the LED chip emits light via its electrodes by which power is supplied to the LED. Thus, some of the emitted light come behind the electrodes, thereby producing a unique, unwanted emission pattern. As a result, the conventional LEDs cannot emit light in all directions in a uniform manner. The LED in accordance with the invention, on the other hand,

does not suffer from such unwanted emission patterns, because light emitted by the LED chip is scattered by the phosphor which allows uniform emission of light from the LED.

[Brief explanation of drawings]

[Fig. 1] Fig. 1 is a schematic cross-sectional view of the present light-emitting diode.

[Fig. 2] Fig. 2 is a schematic cross-sectional view of light-emitting diode other than the present invention.

[Fig. 3] Fig. 3 is an example of light-emission spectrum of the present light-emitting diode.

[Fig. 4] Fig. 4(A) indicates an example of absorption spectrum of photoluminescence fluorescent material employed in the present invention. Fig. 4(B) indicates an example of light-emission spectrum of photoluminescence fluorescent material employed in the present invention.

[Fig. 5] Fig. 5 is a schematic view of LED display device employing the present light-emitting diode.

[Fig. 6] Fig. 6 is a block view of the LED display device employed in Fig. 5.

[Fig. 7] Fig. 7 is a schematic view of another LED display device employing the present light-emitting diode.

[Fig. 8] Fig. 8 (A) indicates lifetime test of comparative example 1 for the comparison with the present Example 1, at a temperature of 25 °C in electric current of 20 mA; Fig. 8(B) is a diagram indicating lifetime test of light-emitting diode of comparative example 1 for the comparison with the present Example 1, under temperature of 60 °C and 90 %RH and in electric current of 20 mA.

[Fig. 9] Fig. 9 is a partial frontal view of a display device wherein, in addition to the present light-emitting diode, light-emitting diodes capable of emitting RGB are arranged as a pixel.

[Fig. 10] Fig. 10(A) indicates light-emission spectrum of photoluminescence fluorescent material of Example 3 expressed by $(Y_{0.6}Gd_{0.4})_3Al_5O_{12}$:Ce.

Fig. 10(B) indicates light-emission spectrum of LED chip of Example 2 having main peak wavelength of 460 nm.

Fig. 10(C) indicates light-emission spectrum of light-emitting diode of Example 2.

[Fig. 11] Fig. 11(A) indicates light-emission spectrum of photoluminescence fluorescent material of Example 5 expressed by $(Y_{0.2}Gd_{0.8})_3Al_5O_{12}$:Ce.

Fig. 11(B) indicates light-emission spectrum of LED chip of Example 5 having main peak wavelength of 450 nm.

Fig. 11(C) indicates light-emission spectrum of light-emitting diode of Example 5.

[Fig. 12]

Fig. 12(A) indicates light-emission spectrum of photoluminescence fluorescent material of Example 6 expressed by $Y_3Al_5O_{12}$:Ce.

Fig. 12(B) indicates light-emission spectrum of LED chip of Example 6 having main peak wavelength of 450 nm.

Fig. 12(C) indicates light-emission spectrum of light-emitting diode of Example 6.

[Fig. 13]

Fig. 13(A) indicates light-emission spectrum of photoluminescence fluorescent material of Example 7 expressed by $Y_3(Al_{0.5}Ga_{0.5})_5O_{12}$:Ce.

Fig. 13(B) indicates light-emission spectrum of LED chip of Example 7 having main peak wavelength of 450 nm.

Fig. 13(C) indicates light-emission spectrum of light-emitting diode of Example 7.

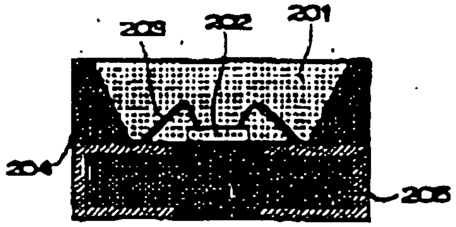
[Symbols in the drawing]

101, 701 ••• coating part containing photoluminescence

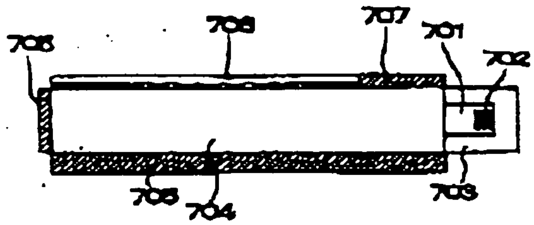
102, 202, 702 ••• LED chip

104 ••• mould member
105 ••• mount lead
106 ••• inner lead
201 ••• mould member containing photoluminescence
204 ••• casing
205 ••• electrodes in the casing
501 ••• light emission diode
504 ••• casing
505 ••• shielding member
506 ••• filler
601 ••• LED display
602 ••• driver
603 ••• RAM
604 ••• gradation controlling means
703 ••• substrate made of metal
704 ••• light guiding plate
705, 707 ••• reflection member
706 ••• scattering sheet

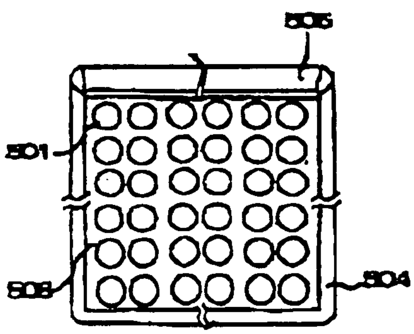
[Fig. 2]



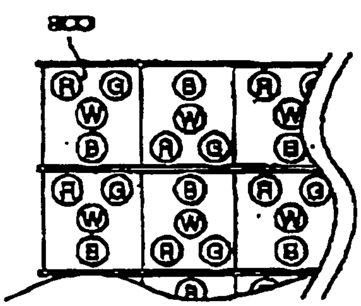
[Fig. 7]



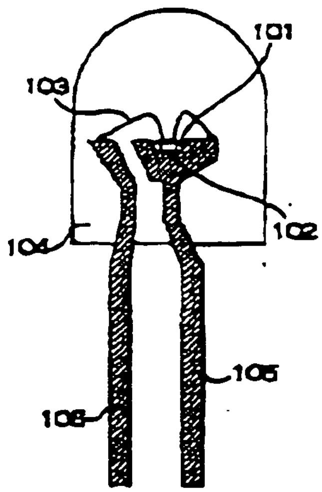
[Fig. 5]



[Fig. 9]

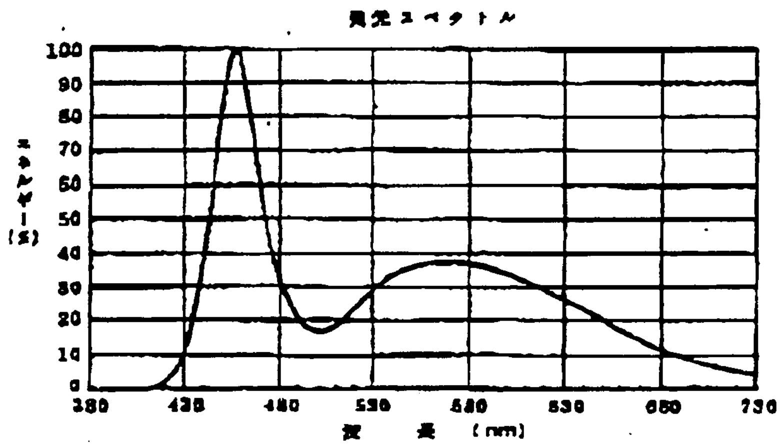


[Fig. 1]



[Fig. 3]

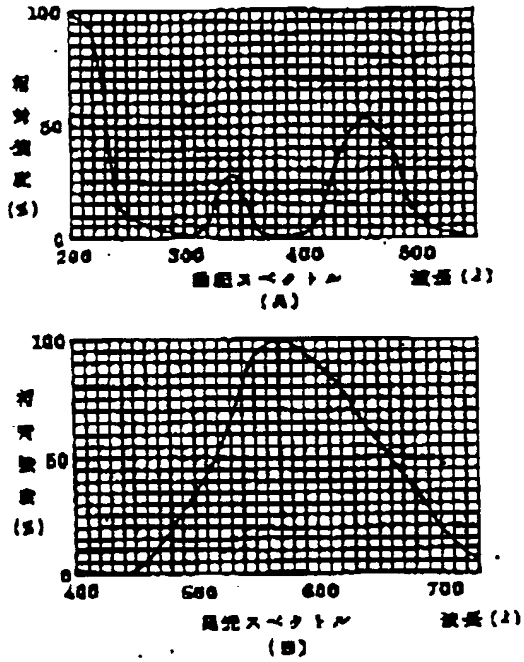
Luminous spectrum



Energy (%)

wavelength (nm)

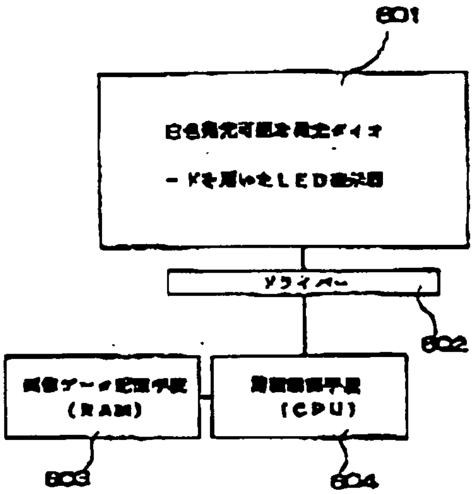
[Fig. 4]



Relative intensity (%)

excitation spectrum wavelength (λ)

[Fig. 6]



601 LED display unit employing a light-emitting diode capable of white light emitting

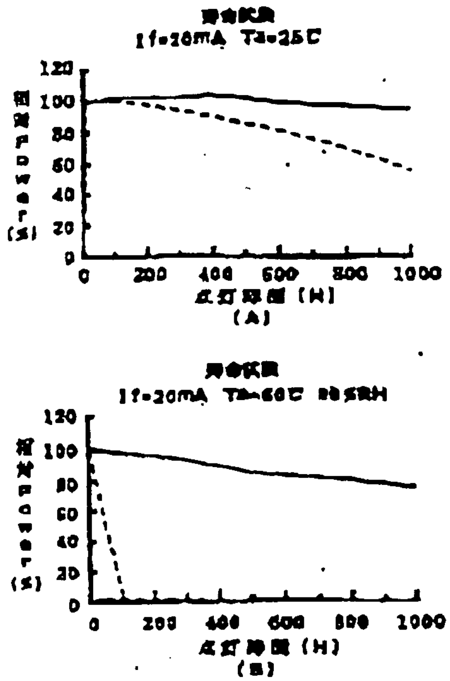
602 Driver

603 Image data storage means (RAM)

604 Gradation control means (CPU)

[Fig. 8]

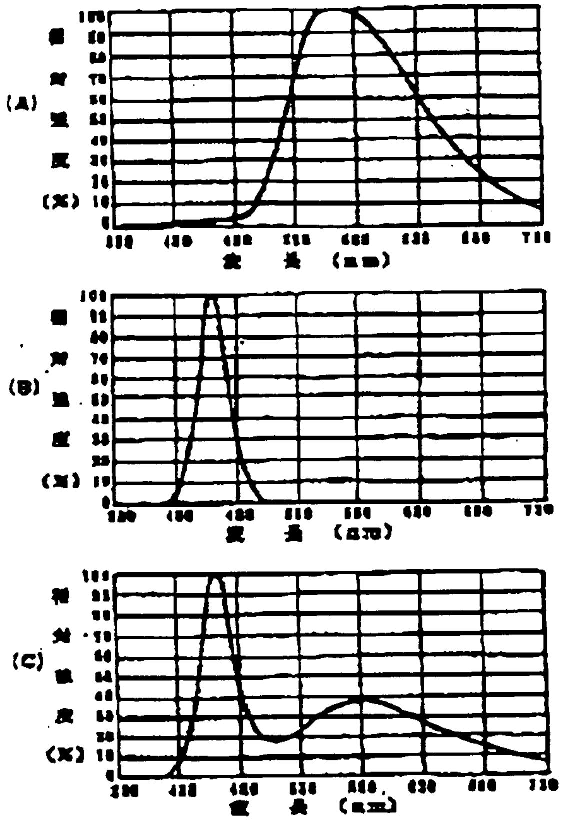
lifetime test



relative Power (%)

Lighting period (H)

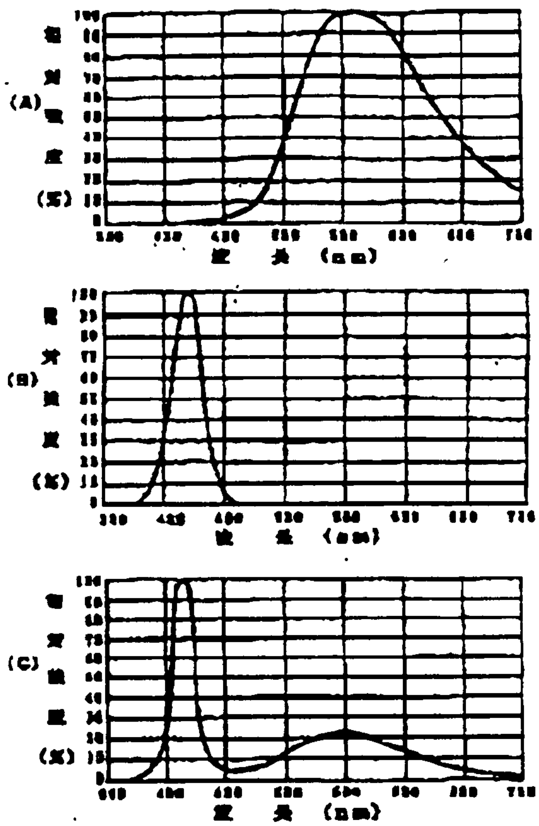
[Fig. 10]



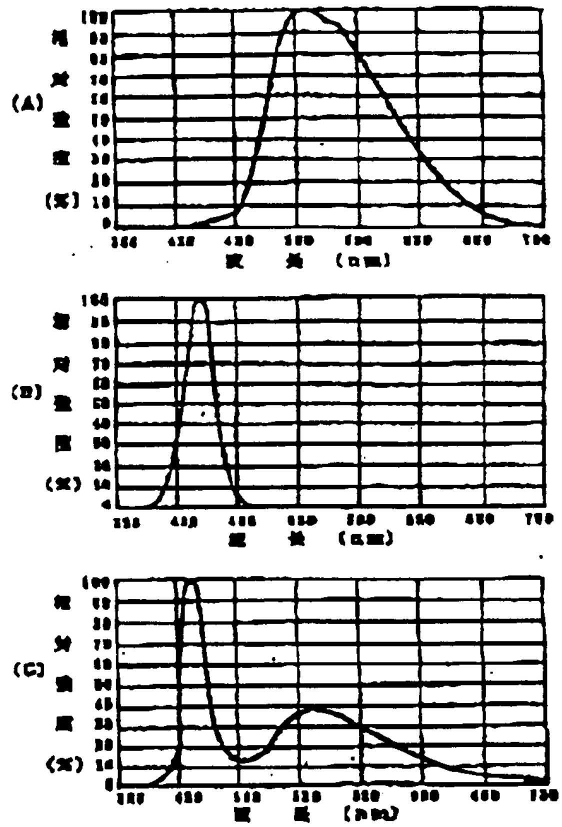
relative intensity (%)

wavelength (nm)

[Fig. 11]



[Fig. 12]



[Fig. 13]